spectra were obtained with a 4.0-μs (30°) pulse, a 15-kHz spectral window, quadrature detection, and 16K data points to give 0.92-Hz data point resolution. Free induction decays were weighted to give 1-Hz line broadening. ^{13}C chemical shifts reported in Table I were obtained from the one-dimensional ^{13}C spectrum and are referenced relative to $CDCl_3$ having a chemical shift of 77.0 ppm. All other chemical shifts and coupling constants were obtained from the 2D-FT NMR spectrum unless otherwise noted.

2D-FT NMR spectra were obtained with HET2DJ and HETCOR pulse sequences supplied in the instrument manufacturer's software package. These sequences cycle the phases of the spectra in order to provide the equivalent of quadrature phase detection in both frequency dimensions. Spectra were obtained in the unlocked mode using a sweep width of 3200 Hz (^{13}C range to cover the upfield portion of the spectrum), 1024 points, 13-μs (90°) ^{13}C and 50-μs (90°) ^1H pulse widths, 0.16-s acquisition time, and 2-s repetition rate. A total of 256 spectra (consisting of 32 transients each) were obtained by varying the evolution time between pulses to provide the equivalent of a 750-Hz sweep width in the second frequency dimension. The free induction decays in the second dimension (obtained by Fourier transformation of each of the 256 spectra followed by transposition of the data matrix) were zero filled to 1024 points and Fourier transformed to provide 1.5 Hz/point resolution in the second dimension (J_{CH} or $^1H\delta$). Spectra were displayed in the absolute value mode to avoid phasing problems. Free induction decays in both dimensions were resolution enhanced and Gaussian weighted ($e^{t/0.04}$ and apodization function = 0.08, respectively) to minimize line broadening and spectral distortion effects caused by the use of the absolute value display mode.

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Utilization of Vinylsilanes in [4 + 2] Cycloaddition Reactions

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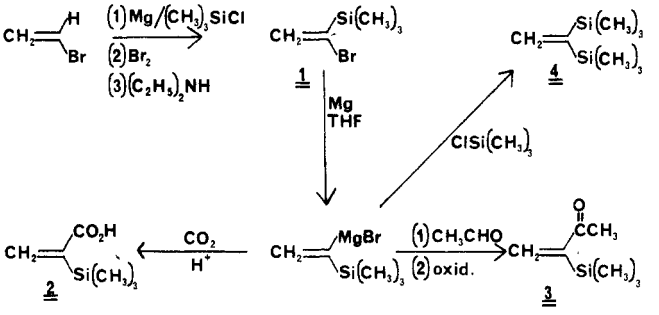
The reaction of several vinylsilanes with benzonitrile oxide, 2-diazopropane, *C*-carboethoxy-*N*-phenylnitrile imine, and substituted 1,3-butadienes has been examined. The 1,3-dipolar cycloadditions followed frontier orbital predictions and gave silylated isoxazoles, nonsilylated pyrazolines, and silylated pyrazolines, respectively. The orientation observed can be explained in terms of maximum orbital overlap of the dipole LUMO–vinylsilane HOMO. The [4 + 2] cycloaddition of several dienes with (2-nitrovinyl)trimethylsilane gave Diels–Alder adducts in good yield. Relative rates for some of the cycloadditions were determined.

In recent years, the utilization of silicon-based reagents has increased greatly in various synthetic transformations.[1-3] Allyltrialkylsilanes have been intensively studied because of their ability to undergo reactions with electrophiles to form carbon–carbon or other bonds with a concomitant double bond shift and cleavage of silicon.[1-3] Vinylsilanes have also been shown to be versatile synthetic intermediates undergoing electrophilic desilylation with retention of stereochemistry.[4-11] These compounds can serve as useful precursors for carbonyl compounds, vinyl halides, and olefins of predictable geometry. Despite their extensive use in organic synthesis, vinylsilanes have been infrequently employed in [4 + 2] cycloaddition reactions. Only occasional examples have been reported that make use of these substrates in Diels–Alder reactions.[12,13] Our interest in utilizing 1,3-dipolar cycloadditions in organic synthesis[14,15] focused our attention on the reaction of various 1,3-dipoles with vinylsilanes.[16] In this paper we wish to describe the results of a study of the profiles of reactivity of several easily accessible 1,3-dipoles toward cycloaddition with a selection of vinylsilanes bearing electron-withdrawing groups.

Results and Discussion

While 1,3-dipolar cycloadditions of nitrile oxides to electron-deficient alkenes have been of extensive value in organic synthesis, the low regioselectivity in the reactions with simple olefins has detracted from the synthetic method. We thought that one approach to circumvent this complication would be to utilize α-silyl-substituted dipolarophiles that undergo regiospecific cycloaddition. This

Scheme I



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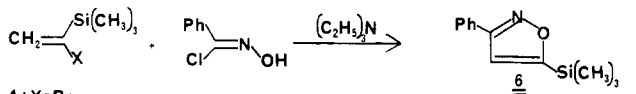
would be followed by cleavage of the silicon group under mild conditions to afford cycloadducts of the parent system. In this paper the effect of a trimethylsilyl group in directing regiospecific cycloaddition of nitrile oxides and the desilylation of these adducts under mild conditions has been studied.

Although there are several methods in the literature for the preparation of vinylsilane derivatives, we found that the Grignard reagent of α-bromovinyltrimethylsilane offered the greatest potential for the one-pot synthesis of α-substituted vinylsilanes in good yield.

On treatment of a carbon tetrachloride solution of either (α-bromovinyl)trimethylsilane (1)[17] or (α-((2,4-dinitrophenyl)thio)vinyl)trimethylsilane[18] (5) and benzohydroximoyl chloride with an excess of triethylamine at 0 °C for 2 h, a high yield of 3-phenyl-5-(trimethylsilyl)-isoxazole (6) was obtained. The structure of 6 was as-

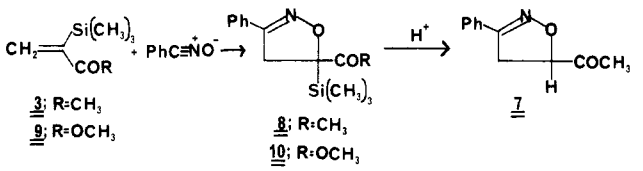


1; X = Br

5; X = $SC_6H_3(NO_2)_2$

signed on the basis of its spectral data as well as by its desilylation with cesium fluoride to give the known 3-phenylisoxazole.[19] The formation of 6 can be postulated to arise by an initial 1,3-dipolar cycloaddition of the transient nitrile oxide followed by elimination of the HX functionality.

In contrast to the above results the reaction of in situ generated benzonitrile oxide with (α-acetylvinyl)trimethylsilane (3) under similar reaction conditions gave 5-acetyl-3-phenylisoxazoline (7). The structure of this



3; R = CH_3

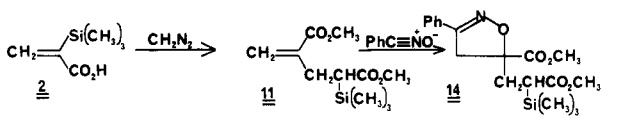
9; R = OCH_3

8; R = CH_3

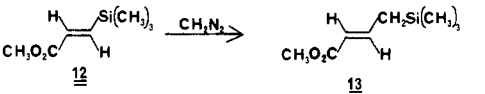
10; R = OCH_3

material was unambigously confirmed by an independent synthesis, which was accomplished by reacting benzonitrile oxide with methyl vinyl ketone. The formation of 7 presumably proceeds by way of cycloadduct 8 which undergoes ready loss of the activated trimethylsilyl group.

Treatment of benzonitrile oxide (generated in situ) with methyl α-(trimethylsilyl)acrylate gave the expected cycloadduct 10, which was easily characterized from its spectral and analytical data (see Experimental Section). During the course of these studies we found that treatment of 2-(trimethylsilyl)acrylic acid with an excess of diazomethane in ether at 0 °C produced 2,4-dicarbomethoxy-4-(trimethylsilyl)-1-butene (11) in high yield. The chemistry of this system differs markedly from that of its β-isomer 12, which has been reported to give the insertion product 13 on treatment with diazomethane.[20] The formation of 11 can be postulated to arise by an initial desilylation (possibly by the basic media present in the ethereal diazomethane) of the vinylsilane to give an allenic



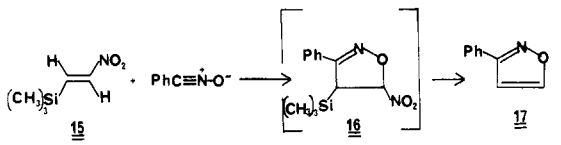
2 → 11 → 14



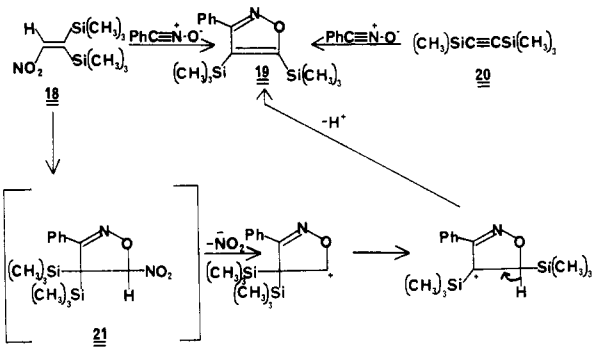
12 → 13

enolate, which subsequently undergoes Michael addition to another molecule of starting material. Treatment of 11 with in situ generated benzonitrile oxide gave isoxazole 14, whose structure was assigned on the basis of its analytical and spectral data: NMR (90 MHz, benzene-d_6) δ 0.20 (s, 9 H), 2.32 (dd, 1 H, J = 16.0 and 8.0 Hz), 2.72 (dd, 1 H, J = 16.0 and 6.0 Hz), 3.10 (s, 2 H), 3.22 (s, 3 H), 3.39 (s, 3 H), 3.78 (dd, 1 H, J = 8.0 and 6.0 Hz), and 7.1–7.8 (m, 5 H); MS, m/e 363 (M^+), 291, 228, 200, and 146.

We also studied the cycloaddition of benzonitrile oxide (generated in situ) with several nitro-substituted vinylsilanes. The nitrovinylsilanes were easily prepared by treating vinylsilane with nitryl chloride[21] followed by base elimination of HCl from the resulting chloronitrosilane. Treatment of (2-nitrovinyl)trimethylsilane (15) with benzonitrile oxide gave 3-phenylisoxazole. In contrast, the reaction of 1,1-bis(trimethylsilyl)-2-nitroethylene (18) with this dipole produced 4,5-bis(trimethylsilyl)-3-phenylisoxazole (19) in 70% yield. The structure of 19 was



15 → 16 → 17



18 → 19; 20

unambiguously established by comparison with an independently synthesized sample prepared from bis(trimethylsilyl)acetylene.[22] The formation of 19 can be postulated to arise by initial formation of cycloadduct 21 followed by loss of the nitro group,[23] 1,2-migration of a trimethylsilyl functionality, and subsequent proton loss. Similarly, loss of the nitro group from cycloadduct 16 followed by desilylation nicely rationalizes the formation of 3-phenylisoxazole from the reaction of 15 with benzonitrile oxide. The isolation of 17 in good yield also illustrates the fact that (2-nitrovinyl)trimethylsilane can serve as an acetylene equivalent in the 1,3-dipolar cycloaddition reaction with benzonitrile oxide. One additional point

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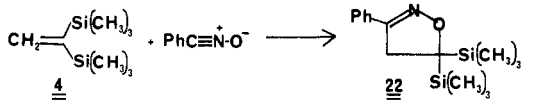
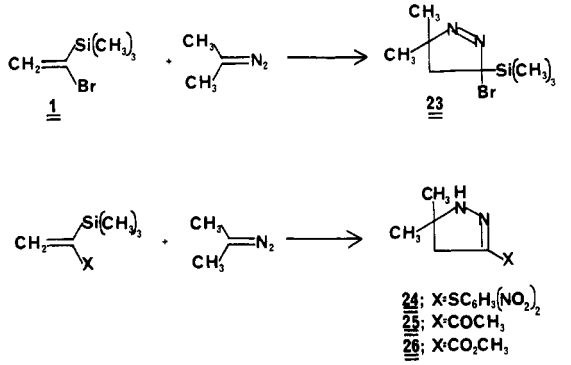
worth noting is that the reaction of benzonitrile oxide with 1,1-bis(trimethylsilyl)ethylene (**4**) gave isoxazoline **22** in 78% yield. This cycloadduct is perfectly stable to silica



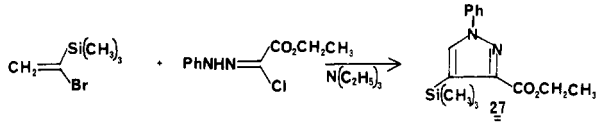
gel chromatography and does not desilylate even under forcing conditions (i.e., cesium fluoride in wet acetonitrile). It would seem that the presence of the nitro group in **18** has a major effect on the regiochemistry of the 1,3-dipolar cycloaddition.

As an extension of our studies dealing with the use of silicon-based reagents as dipolarophiles, we decided to examine the cycloaddition behavior of 2-diazopropane with several vinylsilanes. Treatment of an ethereal solution of 2-diazopropane with (α-bromovinyl)silane (**1**) at 0 °C gave 3-bromo-5,5-dimethyl-3-(trimethylsilyl)pyrazoline (**23**) as the exclusive product. In contrast, however, the reaction

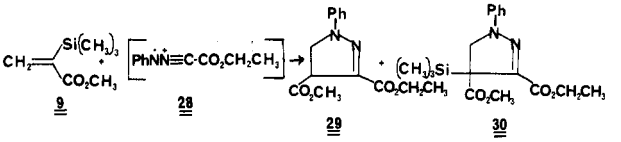


of (α-((2,4-dinitrophenyl)thio)vinyl)trimethylsilane (**5**) with the dipole under similar conditions gave pyrazoline **24**. The structure of this product was unambiguously established by comparison with an independently synthesized sample prepared by treating 2-diazopropane with 2,4-dinitrophenyl vinyl sulfide.[18] Related results were obtained when either (α-acetovinyl)trimethylsilane (**3**) or methyl α-(trimethylsilyl)acrylate was treated with this dipole. The formation of these pyrazolines can be postulated to arise by initial formation of the expected cycloadduct followed by ready loss of the trimethylsilyl group with concomitant protonation on the nitrogen atom.

We have also investigated the cycloaddition behavior of several vinylsilanes with a representative nitrilimine, a long-known and thoroughly investigated 1,3-dipole.[24] The cycloadditions of simple nitrilimines with electron-rich dipolarophiles are LU(1,3-dipole)–HO(dipolarophile) controlled.[25] For conjugated dipolarophiles, both HO and LU interactions are important, but the greater difference in LU coefficients leads to a preference for 5-substituted Δ^2-pyrazolines.[25] With electron-deficient dipolarophiles the regioselectivity is reversed since the cycloaddition becomes HO(1,3-dipole)–LU(dipolarophile) controlled. Treatment of an ethereal solution of (α-bromovinyl)trimethylsilane and ethyl chloro(phenylhydrazono)acetate with an excess of triethylamine produced ethyl *N*-phenyl-4-(trimethylsilyl)pyrazole-3-carboxylate (**27**) in good yield. Reaction of the nitrilimine with methyl α-(trimethylsilyl)acrylate under similar conditions gave a mixture of 3-carbethoxy-4-carbomethoxy-1-phenyl-2-pyrazoline (**29**, 60%) and 3-carbethoxy-4-carbomethoxy-



1-phenyl-4-(trimethylsilyl)-2-pyrazoline (**30**, 34%) as the two major products. Again the silyl group seems to be



very labile with regard to replacement by a proton. This is undoubtedly related to the presence of both the carbomethoxy and imine functionalities.

Numerous rate studies have been reported for the cycloaddition of 1,3-dipoles to alkenes and alkynes.[26] From these studies it has been concluded that each class of 1,3-dipoles exhibits a characteristic dipolarophile activity sequence with relatively minor variation for individual 1,3-dipoles within each class. As part of our interest in using vinylsilanes as reagents for dipolar cycloaddition, we thought it worthwhile to determine the order of reactivity of several representative systems. Generation of the dipole in the presence of a mixture of dipolarophiles creates a competitive system from which the ratio of rates, $K_{rel} = K_B/K_A$, may be obtained by standard treatment of the kinetic data. In order to calculate K_{rel} it is necessary to know the initial concentration of each of the competing dipolarophiles and the concentration of each at a subsequent stage in the reaction. In principle, the data may be determined either directly by measuring the amount of dipolarophile remaining or indirectly from a knowledge of the concentration of reaction products. The former method was used in this study.

$$K_{rel} = \frac{K_{olefinB}}{K_{olefinA}} = \frac{\log ([O_B]_i/[O_B]_f)}{\log ([O_A]_i/[O_A]_f)}$$

The "U-shaped" reactivity curve exhibited by benzonitrile oxide with various alkenes is evidence for a significant contribution from both the HOMO and LUMO of the nitrile oxide in the cycloaddition pathway.[27] Sustmann has classified such 1,3-dipoles as belonging to the type II category.[28] With the trimethylsilyl-substituted alkenes used, benzonitrile oxide reacts with high regioselectivity to give 5-substituted isoxazoles. This orientation can be explained in terms of maximum orbital overlap of the nitrile oxide LUMO–vinylsilane HOMO.[25] Table I shows the order of reactivity of the various vinylsilanes employed in this study. It can be seen that the silylated alkene bearing the acetyl group is approximately 9 times more reactive than the one bearing the carbomethoxy group. The silyl group also reduces the reactivity of the alkene toward the nitrile oxide and hence the non-silyl alkene is slightly more reactive in the cycloaddition reaction (see Table II). It should be pointed out that reactivity (in terms of rates) still appears to be HOMO (benzonitrile oxide)–LUMO (vinylsilane) controlled even if the orientation is LUMO (benzonitrile oxide)–HOMO (vinylsilane) controlled.

The nitrilimine orbitals are similar in energy to those of nitrile oxide, except that the degeneracies of the π-orbitals in the latter are split and the orbitals of the former

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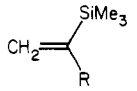
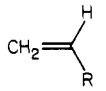
Table I. Reactivity of Various Vinylsilanes toward Benzonitrile Oxide



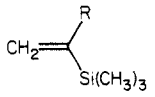
R	CO_2CH_3	Br	SDNB	$COCH_3$
k	1	3	7	9

Table II



R	CO_2CH_3	SDNB	COMe	Br
k_H/k_{SiMe_3}	1.7	1.5	1.2	1.0

Table III. Relative Reactivity of Vinylsilane toward 2-Diazopropane

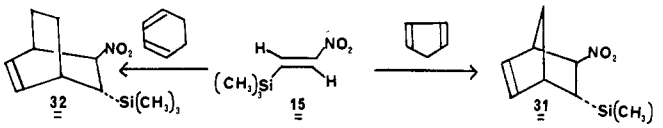


R	CO_2CH_3	Br	$SC_6H_3(NO_2)_2$	$COCH_3$
k	1	2	4	11

are moved to higher energies. With electron-deficient dipolarophiles, both HO and LU interactions are important, but with weakly electron-deficient dipolarophiles, the 5-substituted product is favored. The formation of cycloadducts **27–29** from the reaction of nitrilimine **28** with the vinylsilanes is perfectly compatible with frontier molecular orbital theory. Moreover, the dipolar cycloaddition of vinylsilanes with nitrilimines as well as with nitrile oxides offers a convenient and efficient way to synthesize functionalized pyrazolines and isoxazolines.

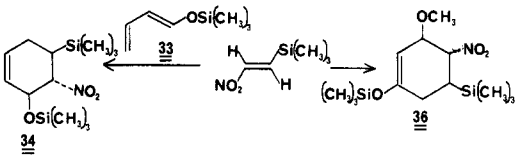
1,3-Dipolar cycloadditions of diazoalkanes to olefins are among the most thoroughly studied examples.[29] The cycloadditions of simple diazoalkanes are HO(1,3-dipole)–LU(dipolarophile) controlled.[25,28] Both conjugating and electron-attracting groups accelerate reactions of dipolarophiles with diazoalkanes as compared to ethylene. With these dipolarophiles, 3-substituted Δ^1-pyrazolines are favored, a result of the union of the larger diazoalkane HO coefficient on carbon with that of the larger dipolarophile LU coefficient on the unsubstituted carbon.[25] Recently, it has been shown that 3-substituted pyrazolines are formed as the major products in the 1,3-dipolar cycloaddition of diazomethane with 1-alkenes.[24,30] With these systems, the difference between the two frontier orbital interactions is quite small, but the nearly equal magnitude of the terminal coefficients in the diazomethane LU suggests that the diazomethane HO determines product regiochemistry. Table III gives the order of reactivity of several vinylsilanes toward 2-diazopropane. The relative order is essentially the same as that found for benzonitrile oxide. The competition studies indicate that the vinylsilane bearing the acetyl group is an order of magnitude more reactive than the silane bearing the carbomethoxy group. This reactivity pattern is to be expected since diazoalkane cycloadditions are HO controlled; they react more rapidly with electron-deficient olefins.

In addition to 1,3-dipolar cycloadditions, the Diels–Alder reactions of silyl-substituted alkenes with reactive π components can be of broad utility in the construction of functionalized ring systems. Our interests in utilizing these cycloadditions in organic synthesis caused us to focus our attention on the [4 + 2] cycloaddition of several dienes with (2-nitrovinyl)silane (**15**). When a benzene solution of **15** and cyclopentadiene was heated at 120 °C, a good yield of the Diels–Alder cycloadduct **31** was produced.



The formation of an analogous product occurred (i.e., **32**) when **15** was heated with 1,3-cyclohexadiene at 178 °C. Unfortunately, all attempts to desilylate these two products were unsuccessful.

We also examined the thermal cycloaddition of (2-nitrovinyl)silane (**15**) with 1-((trimethylsilyl)oxy)butadiene (**33**) and Danishefsky's diene **35**. The thermal addition of **15** to **33** gives cycloadduct **34** in high yield. Diene **35** exhibits similar behavior producing the Diels–Alder cycloadduct **36** in good yield. This material could be readily



hydrolyzed to give a mixture of *cis*- and *trans*-1-methoxy-2-nitro-3-(trimethylsilyl)cyclohexan-5-one.

In summary, we have found that vinylsilanes undergo ready cycloaddition with a variety of 4π systems in synthetically useful yield. Unfortunately, the trimethylsilyl group has little effect on both the rate and regiochemical outcome of the dipolar cycloaddition reaction. Further applications of the [4 + 2] cycloaddition reactions of these compounds in organic synthesis are currently under investigation.

Experimental Section[31]

Reaction of (α-Bromovinyl)trimethylsilane (1) with Benzonitrile Oxide. To a stirred solution containing 1.0 g of benzohydroximoyl chloride[32] and 0.86 g of (α-bromovinyl)trimethylsilane (1)[33] in 40 mL of carbon tetrachloride at 0 °C was slowly added 2.0 g of triethylamine. The resulting mixture was stirred at 0 °C for 2 h and was then filtered, and the solvent was removed under reduced pressure. The crude residue was subjected to silica gel chromatography with a 10% ethyl acetate–hexane mixture as the eluent. The major fraction isolated was a colorless oil (0.81 g, 60%) whose structure was assigned as 3-phenyl-5-(trimethylsilyl)oxazole (**6**) on the basis of the following data: IR (neat) 3100, 3000, 2940, 1600, 1550, 1460, 1430, 1390, 1260, 1100, 900, and 760 cm^{-1}, NMR (CCl_4,90 MHz) δ 0.12 (s, 9 H), 6.45 (s, 1 H), and 7.0–7.8 (m, 5 H); m/e 217 (M^+), 174, 126, and 99; UV (cyclohexane) 241 nm (ϵ 11 000).

Anal. Calcd for $C_{12}H_{15}NOSi$: C, 66.32; H, 6.96; N, 6.44. Found: C, 66.42; H, 6.99; N, 6.38.

Reaction of (α-((2,4-Dinitrophenyl)thio)vinyl)trimethylsilane (5) with Benzonitrile Oxide. To a stirred solution containing 1.0 g of benzohydroximoyl chloride and 0.92 g

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(33) Sommer, L. H.; Bailey, D. L.; Goldberg, G. M.; Buck, E. C.; Bye, T. S.; Evans, F. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1954**, *76*, 1613.

of (α-((2,4-dinitrophenyl)thio)vinyl)trimethylsilane (**5**)[18] in 40 mL of carbon tetrachloride at 0 °C was slowly added 2.0 g of triethylamine. The mixture was stirred at 25 °C for 2 h and was filtered. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with a 5% ethyl acetate–hexane mixture as the eluent. The major fraction contained 0.75 g (62%) of 3-phenyl-5-(trimethylsilyl)-isoxazole (**6**) as a clear oil. The structure of this material was verified by a desilylation reaction. To a stirred suspension of 0.18 g of cesium fluoride in 4 mL of acetonitrile and 0.2 mL of ethanol was slowly added 0.19 g of 3-phenyl-5-(trimethylsilyl)isoxazole (**6**) in 0.5 mL of acetonitrile. The solution was stirred for 10 min and was then filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give 0.12 g (82%) of 3-phenylisoxazole (**17**):[19] IR (neat) 3150, 3080, 2950, 1590, 1550, 1445, 1390, 1275, 1120, 1090, 870, and 750 cm^{-1}; NMR (CCl_4, 90 MHz) δ 6.54 (d, 1 H, J = 1.5 Hz), 7.2–7.8 (m, 5 H), and 8.37 (d, 1 H, J = 1.5 Hz); m/e 145, 144, 89, and 77; UV (cyclohexane) 238 nm (ε 16800).

Reaction of (α-Acetylvinyl)trimethylsilane (3) with Benzonitrile Oxide. To a stirred solution of 1.0 g benzohydroximoyl chloride[32] and 0.9 g of **3**[34] in 40 mL of carbon tetrachloride at 0 °C was slowly added 2.0 g of triethylamine. After stirring for 2 h the mixture was filtered and the solvent was removed under reduced pressure. The crude oil was purified by silica gel chromatography to give 0.75 g (63%) of 5-acetyl-3-phenylisoxazole (**7**) as a white solid: mp 61–62 °C; IR (KBr) 3170, 2980, 1720, 1600, 1440, 1350, and 880 cm^{-1}; NMR (CCl_4, 90 MHz) δ 2.30 (s, 3 H), 3.46 (dd, 1 H, J = 15.0 and 11.0 Hz), 3.74 (dd, 1 H, J = 15.0 and 7.0 Hz), 5.05 (dd, 1 H, J = 11.0 and 7.0 Hz), and 7.3–7.8 (m, 5 H); m/e 189 (M^+), 146, 118, 91, and 77; UV (cyclohexane) 275 nm (ε 12600).

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.70; H, 5.88; N, 7.34.

Reaction of Methyl α-(Trimethylsilyl)acrylate (9) with Benzonitrile Oxide. To a stirred solution of 1.0 g benzohydroximoyl chloride[32] and 1.0 g of methyl α-(trimethylsilyl)-acrylate[20] in 40 mL of carbon tetrachloride at 0 °C was slowly added 2.0 g of triethylamine. After the mixture was stirred for 2 h it was filtered and the solvent was removed under reduced pressure. The resulting residue was purified by silica gel chromatography with a 10% ethyl acetate–hexane mixture. The major fraction was sublimed at 100 °C (0.05 mm) to give 1.3 g (74%) of methyl 4,5-dihydro-3-phenyl-5-(trimethylsilyl)isoxazole-5-carboxylate (**10**): mp 60–61 °C; IR (KBr) 3170, 2980, 1720, 1640, 1600, 1440, 1340, 1245, 1155, 1080, 1020, and 830 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.2 (s, 9 H), 3.47 (dd, 2 H, J = 16.0 and 8.0 Hz), 3.57 (s, 3 H), and 7.2–7.7 (m, 5 H); m/e 277, 258, 244, 176, 159, 146, 89, and 78.

Anal. Calcd for $C_{14}H_{19}NO_3Si$: C, 60.62; H, 6.90; N, 5.05. Found: C, 60.68; H, 6.90; N, 5.04.

Reaction of 2,4-Dicarbomethoxy-4-(trimethylsilyl)-1-butene (11) with Benzonitrile Oxide. To a stirred solution of 10 g of diazomethane in 200 mL of ether at 0 °C was slowly added 10.0 g of 2-(trimethylsilyl)acrylic acid (**2**).[35] The resulting solution was stirred at 0 °C for 3 h and was then dried over magnesium sulfate. The solvent was removed under reduced pressure to leave behind a clear oil whose structure is assigned as 2,4-dicarbomethoxy-4-(trimethylsilyl)-1-butene (**11**) on the basis of its spectral properties: IR (neat) 2970, 1740, 1600, 1490, 1430, 1350, 1240, 1160, 1020, 980, 825, 745, and 720 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.2 (s, 9 H), 2.55 (d, 2 H, J = 7.0 Hz), 3.40 (t, 1 H, J = 7.0 Hz), 3.60 (s, 6 H), 5.28 (br s, 1 H), and 5.47 (br s, 1 H); m/e 244 (M^+), 230, 181, 153, and 109; UV (cyclohexane) 215 nm (ε 400).

Anal. Calcd for $C_{11}H_{20}SiO_4$: C, 54.07; H, 8.25. Found: C, 54.18; H, 8.28.

To a stirred solution containing 1.0 g of benzohydroximoyl chloride[32] and 1.0 g of **11** in 60 mL of carbon tetrachloride at 0 °C was slowly added 1.5 g of triethylamine. The mixture was stirred for 2 h and was then filtered. The solvent was removed and the resulting residue was subjected to silica gel chromatography with a 10% ethyl acetate–hexane mixture to give structure **14** as a crystalline solid: mp 79–80 °C; IR (KBr) 2970, 1740, 1600, 1570, 1500, 1440, 1350, 1250, 1200, 1040, 960, 840, 750, and 690 cm^{-1}; NMR (benzene-d_6, 90 MHz) δ 0.2 (s, 9 H), 2.32 (dd, 1 H, J = 16.0 and 8.0 Hz), 2.72 (dd, 1 H, J = 16.0 and 6.0 Hz), 3.10 (s, 2 H), 3.22 (s, 3 H), 3.39 (s, 3 H), 3.78 (dd, 1 H, J = 8.0 and 6.0 Hz), and 7.1–7.8 (m, 5 H); m/e 363, 291, 228, 200, and 146; UV (cyclohexane) 273 nm (ε 12000).

Anal. Calcd for $C_{18}H_{25}NO_5Si$: C, 59.48; H, 6.93; N, 3.85. Found: C, 59.58; H, 6.95; N, 3.84.

Reaction of 2-Nitro-1-(trimethylsilyl)ethylene (15) with Benzonitrile Oxide. To 50 g of vinyltrimethylsilane at 0 °C was slowly added 100 g of nitryl chloride.[21] The resulting brown mixture was stirred at 0 °C for 2 h. The solution was then carefully poured into 100 mL of an ice-cold saturated solution of ammonium chloride. After extraction with ether the extracts were washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 80 g (89%) of 1-chloro-2-nitro-1-(trimethylsilyl)ethane, which was used without further purification. To 80 g of this material in 200 mL of ether at 0 °C was slowly added 56 g of DBN in 50 mL of ether. The solution was stirred at 0 °C for 40 min after which it was poured into 200 mL of an ice-cold 5% hydrochloric acid solution and extracted with ether. The ether solution was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 35 g (61%) of 2-nitro-1-(trimethylsilyl)ethene (**15**) as a yellow oil: bp 70–72 °C (15 mm); IR (neat) 3000, 1640, 1540, 1420, 1360, 1300, 1260, 1185, 1120, 1020, 950, 910, 740, and 680 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.2 (s, 9 H), 6.9 (d, 1 H, J = 15.0 Hz), 7.25 (d, 1 H, J = 15.0 Hz); m/e 131 (M^+) and 105; UV (95% ethanol) 235 nm (ε 1200).

To a stirred solution containing 0.6 g of benzohydroximoyl chloride and 0.5 g of the above nitrosilane in 50 mL of carbon tetrachloride at 0 °C was slowly added 1.5 g of triethylamine. The mixture was stirred for 2 h and was then filtered. The residue was subjected to silica gel chromatography with a 5% ethyl acetate–hexane mixture as the eluent to give 0.15 g (27%) of 3-phenylisoxazole (**17**).[19]

Reaction of 2-Nitro-1,1-bis(trimethylsilyl)ethylene (18) with Benzonitrile Oxide. To a 2.0-g sample of 1,1-bis(trimethylsilyl)ethylene (**4**)[36] at 0 °C was slowly added 5.5 g of nitryl chloride. The mixture was stirred at 0 °C for 2 h. Traditional workup of the mixture gave 1.5 g (51%) of a yellow liquid, which was used without further purification. To 1.0 g of this material in 20 mL of ether at 0 °C was slowly added a solution containing 0.48 g of DBN in 2 mL of ether. The solution was stirred for 2 h followed by the standard workup to give 0.56 g (65%) of 2-nitro-1,1-bis(trimethylsilyl)ethylene (**18**) as a yellow oil: bp 110 °C (12 mm); IR (neat) 3000, 2830, 1640, 1540, 1410, 1340, 1300, 1250, 1060, 960, 840, and 760 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.10 (s, 12 H) and 7.2 (s, 1 H); m/e 203 (M^+) and 177; UV (95% ethanol) 230 nm (ε 1000).

To a stirred solution of 0.3 g of benzohydroximoyl chloride[32] and 0.4 g of 2-nitro-1,1-bis(trimethylsilyl)ethylene (**18**) in 40 mL of carbon tetrachloride at 0 °C was slowly added 1.0 g of triethylamine. The mixture was stirred for 2 h and was then filtered and concentrated under reduced pressure. The resulting oil was purified by silica gel chromatography with a 5% ethyl acetate–hexane mixture to give 0.38 g (69%) of 4,5-bis(trimethylsilyl)-3-phenylisoxazole (**19**): mp 47–48 °C; IR (KBr) 3000, 2950, 1605, 1565, 1460, 1360, 1260, 1080, and 780 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.02 (s, 9 H), 0.37 (s, 9 H), and 7.29 (s, 5 H); m/e 289 (M^+), 274, 246, 200, 171, 147, and 97; UV (cyclohexane) 215 nm (ε 7400).

Anal. Calcd for $C_{15}H_{23}NOSi_2$: C, 62.22; H, 8.01; N, 4.84. Found: C, 61.99; H, 8.13; N, 4.80.

Further support for the structure of **19** was obtained by an independent synthesis from the reaction of benzonitrile oxide with bis(trimethylsilyl)acetylene (**20**).

Reaction of 1,1-Bis(trimethylsilyl)ethylene (4) with Benzonitrile Oxide. To a stirred solution containing 0.45 g of benzohydroximoyl chloride[32] and 0.5 g of 1,1-bis(trimethylsilyl)ethylene (**4**)[36] in 40 mL of carbon tetrachloride at 0 °C was slowly added 2.0 g of triethylamine. The mixture was stirred at 0 °C for 2 h and was then filtered and concentrated under reduced

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pressure. The crude residue was purified by silica gel chromatography with a 10% ethyl acetate–hexane mixture as the eluent to give 0.61 g (78%) of 3-phenyl-5,5-bis(trimethylsilyl)isoxazoline (**22**) as a crystalline solid: mp 56–57 °C; IR (KBr) 3100, 3000, 2940, 2880, 1600, 1570, 1500, 1440, 1410, 1350, 1260, 1080, 1040, 1010, 920, 820, and 690 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.21 (s, 18 H), 3.40 (s, 2 H), and 7.3–7.8 (m, 5 H); *m/e* 219 (M^+), 202, 176, 147, and 73; UV (cyclohexane) 290 nm (ϵ 8200).

Anal. Calcd for $C_{15}H_{25}NOSi_2$: C, 61.80; H, 8.64; N, 4.80. Found: C, 62.02; H, 8.70; N, 4.81.

Reaction of (α-Bromovinyl)trimethylsilane (1) with 2-Diazopropane. To a solution containing 1.5 g of 2-diazopropane[37] in 30 mL of ether at 0 °C was added 0.4 g of (α-bromovinyl)-trimethylsilane (1) in 30 mL of ether. After stirring for 4 h the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with a 10% ethyl acetate–hexane mixture as the eluent to give 0.35 g (63%) of 3-bromo-5,5-dimethyl-3-(trimethylsilyl)pyrazoline (**23**) as a colorless, labile oil; IR (neat) 2980, 2940, 2905, 1530, 1450, 1370, 1260, 1080, 930, 890, 850, 750, and 700 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.28 (s, 9 H), 1.47 (s, 3 H), and 1.87 (dd, 2 H, J = 15.0 and 13.0 Hz); *m/e* 249 (M^+), 207, and 189; UV (95% ethanol) 246 nm (ϵ 4800). As a result of its lability no effort was made to obtain any analytical data.

Reaction of (α-((2,4-Dinitrophenyl)thio)vinyl)trimethylsilane (5) with 2-Diazopropane. To a stirred solution containing 4.0 g of 2-diazopropane[37] in 100 mL of ether at 0 °C was added 1.0 g of **5**. After stirring for 3 h the solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography with a 30% ethyl acetate–hexane mixture to give 0.6 g (53%) of a crystalline solid, mp 111–112 °C, whose structure was assigned as 3-((2,4-dinitrophenyl)thio)-5,5-dimethyl-2-pyrazoline (**24**): IR (KBr) 3380, 3060, 1600, 1520, 1340, 1290, 1215, 1040, and 900 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.40 (s, 6 H), 2.70 (s, 2 H), 5.50 (br s, 1 H), and 7.7–9.2 (m, 3 H); *m/e* 281 ($M^+ - 15$), 235, 234, 189, 147, 130, 113, and 95; UV (95% ethanol) 265 nm (ϵ 21000). The structure of this material was further verified by comparison with an independently synthesized sample prepared from the reaction of 2-diazopropane[37] with 2,4-dinitrophenyl vinyl sulfide.[18]

Reaction of (α-Acetylvinyl)trimethylsilane (3) with 2-Diazopropane. To a stirred solution of 4.0 g of 2-diazopropane[37] in 100 mL of ether at 0 °C was added 1.0 g of (α-acetylvinyl)-trimethylsilane (**3**).[34] After stirring for 2 h the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel chromatography column with a 8% ethyl acetate–hexane mixture as the eluent. The major fraction contained 0.7 g (75%) of a colorless oil whose structure is assigned as 3-acetyl-5,5-dimethyl-2-pyrazoline (**25**) on the basis of its spectral properties: IR (neat) 3320, 2980, 2950, 1640, 1530, 1405, 1260, 1220, 1110, and 750 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.93 (s, 6 H), 1.90 (s, 3 H), 2.20 (s, 2 H), and 5.90 (br s, 1 H); *m/e* 140 (M^+), 125, 177, and 183; UV (cyclohexane) 276 nm (ϵ 15000).

Anal. Calcd for $C_7H_{12}N_2O$: C, 59.97; H, 8.63; N, 19.99. Found: C, 59.89; H, 8.68; N, 19.74.

The structure of **25** was further verified by comparison with an independently synthesized sample prepared by treating 2-diazopropane with methyl vinyl ketone.

Reaction of Methyl α-(Trimethylsilyl)acrylate (9) with 2-Diazopropane. To a stirred solution containing 4.0 g of 2-diazopropane[37] in 100 mL of ether at 0 °C was added 1.0 g of acrylate **9**.[20] The mixture was stirred for 2 h and then the solvent was removed under reduced pressure. Chromatography of the crude reaction mixture on silica gel with a 8% ethyl acetate–hexane mixture gave 0.75 g (76%) of a colorless oil whose structure was assigned as methyl 5,5-dimethyl-2-pyrazoline-3-carboxylate (**26**): IR (neat) 3340, 2970, 1700, 1545, 1440, 1400, 1270, 1225, 1185, 1110, 1070, 960, 820, and 780 cm^{-1}; NMR (CCl_4, 90 MHz) δ 1.23 (s, 6 H), 2.63 (s, 2 H), 2.72 (s, 3 H), and 6.90 (br s, 1 H); *m/E* 156 (M^+), 141, 125, 110, 97, and 67; UV (cyclohexane) 287 nm (ϵ 15000).

Anal. Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.78; H, 7.65; N, 17.82.

The structure of **26**, was further verified by comparison with an independently synthesized sample prepared by treating 2-diazopropane with methyl acrylate.

Reaction of (α-Bromovinyl)trimethylsilane (1) with Ethyl Chloro(phenylhydrazono)acetate in the Presence of Base. To a solution containing 1.68 g of ethyl chloro(phenylhydrazono)acetate[38] and 1.0 g of (α-bromovinyl)trimethylsilane (1)[39] in 160 mL of ether at 25 °C was added 4.0 g of triethylamine. After stirring for 48 h the mixture was filtered and the solvent was removed under reduced pressure. The resulting oil was chromatographed on a silica gel column with a 10% ethyl acetate–hexane mixture as the eluent. The major component contained 1.0 g (47%) of a colorless oil, bp 110 °C (0.06 mm), whose structure was assigned as ethyl 1-phenyl-4-(trimethylsilyl)-pyrazole-3-carboxylate (**27**) on the basis of its spectral data: IR (neat) 3000, 1720, 1600, 1500, 1400, 1340, 1240, 1205, 1110, 1020, 1000, 840, 820, and 680 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.02 (s, 9 H), 1.43 (t, 3 H, J = 7.0 Hz), 4.38 (q, 2 H, J = 7.0 Hz), 7.00 (s, 1 H), and 7.51 (s, 5 H); *m/e* 288 (M^+), 273, 243, 228, 216, 171, and 144; UV (95% ethanol) 244 nm (ϵ 7600).

Anal. Calcd for $C_{14}H_{20}N_2O_2Si$: C, 62.47; H, 6.99; N, 9.71. Found: C, 62.53; H, 7.02; N, 9.70.

Reaction of Methyl α-(Trimethylsilyl)acrylate (9) with Ethyl Chloro(phenylhydrazono)acetate in the Presence of Base. To a solution containing 0.72 g of the hydrazonoacetate and 0.5 g of methyl α-trimethylsilylacrylate in 50 mL of ether was added 4.0 g of triethylamine. After stirring for 48 h the solution was filtered and concentrated under reduced pressure. The resulting oil was subjected to silica gel chromatography with a 10% ethyl acetate–hexane mixture as the eluent. The major fraction contained 0.66 g (60%) of a clear oil whose structure was assigned as 3-carbethoxy-4-carbomethoxy-1-phenyl-4-(trimethylsilyl)-2-pyrazoline (**30**) on the basis of its spectral properties: IR (neat) 3000, 1720, 1600, 1560, 1490, 1420, 1300, 1240, 1140, 1100, 1010, 820, and 745 cm^{-1}; NMR (CCl_4, 60 MHz) δ 0.01 (s, 9 H), 1.18 (t, 3 H, J = 7.0 Hz), 3.26 (s, 2 H), 3.52 (s, 3 H), 4.05 (q, 2 H, J = 7.0 Hz), and 6.8–7.2 (m, 5 H); *m/e* 348 (M^+), 303, 287, 276, 229, 217, 199, and 171; UV (95% ethanol) 349 (ϵ 15400), 298 (ϵ 4000), and 236 nm (ϵ 9800).

Anal. Calcd for $C_{17}H_{24}N_2O_4Si$: C, 58.59; H, 6.94; N, 8.04. Found: C, 58.38; H, 6.90; N, 8.03.

The minor component isolated from the column was a colorless oil (0.3 g, 34%) whose structure was assigned as 3-carbethoxy-4-carbomethoxy-1-phenyl-2-pyrazoline (**29**) on the basis of its spectral data: IR (neat) 3000, 1740, 1700, 1600, 1560, 1500, 1440, 1345, 1300, 1245, 1140, 1100, 1060, 1000, 760, and 740 cm^{-1}; NMR (CCl_4, 60 MHz) δ 1.40 (t, 3 H, J = 7.0 Hz), 3.52 (m, 2 H), 3.70 (s, 3 H), 4.29 (q, 2 H, J = 7.0 Hz), 4.85 (dd, 1 H, J = 12.0 and 9.0 Hz), and 6.8–7.4 (m, 5 H); *m/e* 276 (M^+), 231, 229, 217, 171, and 145; UV (95% ethanol) 350 (ϵ 17000), 297 (ϵ 3400), and 236 nm (ϵ 9100).

Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 61.16; H, 5.93; N, 9.78.

Reaction of (2-Nitrovinyl)trimethylsilane with Cyclopentadiene. A solution containing 400 mg of (2-nitrovinyl)trimethylsilane and 400 mg of dicyclopentadiene in 1 mL of benzene was heated in a sealed tube at 120 °C for 50 h. The solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column with a 30% ethyl acetate–hexane mixture as the eluent. The major fraction contained 500 mg (80%) of a clear oil whose structure was assigned as 2-nitro-3-(trimethylsilyl)bicyclo[2.2.1]hept-2-ene (**31**) on the basis of its spectral properties: IR (neat) 3020, 1640, 1545, 1370, 1335, 1250, 1180, 1140, 1054, 950, 865, 824, 760, and 710 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.12 (s, 9 H), 1.2–1.7 (m, 3 H), 2.90 (br s, 1 H), 3.60 (br s, 1 H), 4.82 (dd, 1 H, J = 10.0 and 7.0 Hz), 5.90 (dd, 1 H, J = 12.0 and 6.0 Hz), and 6.55 (dd, 1 H, J = 12.0 and 6.0 Hz); *m/e* 165, 138, 92, and 73.

Anal. Calcd for $C_{10}H_{17}NO_2Si$: C, 56.83; H, 8.11; N, 6.63. Found: C, 56.95; H, 8.17; N, 6.71.

Reaction of (2-Nitrovinyl)trimethylsilane with 1,3-Cyclohexadiene. A solution containing 0.4 g of 1,3-cyclohexadiene and 0.3 g of (2-nitrovinyl)trimethylsilane in 1 mL of

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benzene was heated in a sealed tube at 178 °C for 19 h. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column with a 30% ethyl acetate–hexane mixture as the eluent to give 0.4 g (83%) of a clear oil whose structure was assigned as 2-nitro-3-(trimethylsilyl)bicyclo[2.2.2]oct-5-ene (**32**) on the basis of the following data: bp 80–81 °C (0.04 mm); IR (neat) 3100, 3020, 1620, 1550, 1460, 1310, 1255, 1160, 1035, 880, 840, 740, and 685 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.10 (s, 9 H), 1.0–1.7 (m, 5 H), 3.70 (m, 1 H), 3.35 (, 1 H), 4.45 (m, 1 H), 6.00 (t, 1 H, J = 6.0 Hz), and 6.52 (t, 1 H, J = 6.0 Hz); m/e 195, 179, 152, 135, 126, 106, and 78.

Anal. Calcd for $C_{11}H_{19}NO_2Si$: C, 58.63; H, 8.50; N, 6.21. Found: C, 58.74; H, 8.55; N, 6.15.

Reaction of (2-Nitrovinyl)trimethylsilane with 1-((Trimethylsilyl)oxy)butadiene (33). A solution containing 250 mg of **33** and 250 mg of (2-nitrovinyl)trimethylsilane in 2 mL of benzene was heated in a sealed tube at 100 °C for 37 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with a 30% ethyl acetate–hexane mixture. The major fraction contained 420 mg (83%) of a clear oil whose structure was assigned as 1-nitro-2-(trimethylsilyl)-6-((trimethylsilyl)oxy)cyclohex-4-ene (**34**) on the basis of its spectral data: IR (neat) 3000, 1640, 1550, 1420, 1370, 1300, 1250, 1160, 1100, 1070, 1035, 840, 740, and 680 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.15 (s, 9 H), 0.20 (s, 9 H), 1.9–2.3 (m, 3 H), 3.49 (s, 3 H), and 3.5–5.1 (m, 3 H); m/e 272, 241, 168, 151, 147, 142, and 103. This material was quite sensitive to moisture and consequently did not analyze properly.

Reaction of (2-Nitrovinyl)trimethylsilane with *trans*-1-Methoxy-3-((trimethylsilyl)oxy)-1,3-butadiene (35). A solution containing 200 mg of **35** and 200 mg of (2-nitrovinyl)trimethylsilane in 1 mL of benzene was heated in a sealed tube at 100 °C for 20 h. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography with a 30% ethyl acetate–hexane mixture as the eluent. The major fraction contained 300 mg (85%) of a colorless oil whose structure was assigned as 1-methoxy-2-nitro-3-(trimethylsilyl)-5-((trimethylsilyl)oxy)cyclohex-5-ene (**36**) on the basis of its spectral data: IR (neat) 3000, 2850, 1660, 1550, 1420, 1300, 1250, 1200, 1080, 1010, 835, and 740 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.17 (s, 9 H), 0.34 (s, 9 H), 1.6–2.3 (m, 2 H), 3.37 (s, 3 H), and 3.8–5.2 (m, 4 H); m/e 302, 271, 257, 244, 167, 151, 141, 125, 109, 97, and 73.

The structure of this material was further verified by an aqueous acid hydrolysis. To a solution containing 150 mg of **36** in 20 mL of tetrahydrofuran was added 4 mL of a 5% aqueous acetic acid solution. After stirring for 1 h the solution was poured into 60 mL of ice–water and extracted several times with ether. The combined ether extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The crude reaction mixture was subjected to silica gel chromatography with a 30% ethyl acetate–hexane mixture. The two major fractions isolated corresponded to *cis*- (67%) and *trans*-1-methoxy-2-nitro-3-(trimethylsilyl)cyclohexan-5-one (26%). The cis isomer (**37**) was a clear oil: bp 60–61 °C (0.04 mm); IR (neat) 3000, 1722, 1550, 1420, 1360, 1240, 1180, 1080, 1020, 980, 840, and 740 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.12 (s, 9 H), 1.8–2.9 (m, 5 H), 3.40 (s, 3 H), 4.10 (m, 1 H), and 4.86 (dd, 1 H, J = 8.0 and 3.0 Hz); m/e 230, 199, 185, 167, 151, 141, and 125.

Anal. Calcd for $C_{10}H_{19}NO_4Si$: C, 48.95; H, 7.81; N, 5.71. Found: C, 49.18; H, 7.86; N, 5.76.

The trans isomer (**38**) was a crystalline solid: mp 59–60 °C; IR (KBr) 2965, 1720, 1550, 1420, 1370, 1320, 1240, 1180, 990, 970, and 830 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.12 (s, 9 H), 1.0–2.9 (7, 5 H), 3.31 (s, 3 H), 3.90 (m, 1 H), and 4.60 (dd, 1 H, J = 12.0 and 9.0 Hz); m/e 230, 199, 185, 167, 151, 141, 125, 104, and 85.

Anal. Calcd for $C_{10}H_{19}NO_4Si$: C, 48.95; H, 7.81; N, 5.71. Found: C, 49.03; H, 7.89; N, 5.66.

Competitive Reactivity Studies. Relative reactivity studies were carried out on mixtures of two different dipolarophiles, an internal standard, and a solution containing 0.5 g of benzohydroximoyl chloride in 20 mL of carbon tetrachloride at 0 °C. To this mixture was slowly added 2.0 g of triethylamine; the resulting mixture was stirred at 0 °C for 2 h and was then filtered, and the solvent was removed under reduced pressure. The relative reactivities were determined by gas chromatography or quantitative NMR spectroscopy using the relation

$$k_{rel} = \log (A/A_0)/\log (B/B_0)$$

where A_0 and B_0 are the areas of the two dipolarophiles relative to the internal standard prior to the reaction and A and B are the same quantities after reaction. The final peak areas were determined by GLC after ca. 40% of the dipolarophiles had been consumed. The relative rate differences are good to ±10%.

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Boron Trifluoride Promoted Reaction of Alkyl Hypohalites with Alkenes. A New Synthesis of Fluoro Halides

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The reactions of the following alkenes with alkyl hypohalites and boron trifluoride (BF_3) were investigated: cyclohexene (**3**), 1-hexene (**8**), *trans*-1,2-dichloroethylene (**15**), methyl acrylate (**18**), methyl crotonate (**25**), methyl isocrotonate (**29**), butadiene (**33**), methyl vinyl ketone (**42**), and styrene (**45**). Reactions of these alkenes with methyl hypochlorite (**1**) and BF_3 in dichloromethane give fluoro chloride adducts as well as methoxy chlorides with the percentage of fluoro chlorides varying from 75% for **29** to 8% for **45**. Fluoro bromide adducts are obtained with methyl hypobromite (**2**). Reactions with the *tert*-butyl hypohalites and BF_3 also give fluoride incorporation. The percentage of fluoride incorporation with **1** or **2** is significantly greater in carbon tetrachloride than in dichloromethane.

Although alkyl hypohalites are well-known for radical reactions with alkenes,[1] their potential for ionic reactions has received less attention. Hypohalites react with alkenes by ionic mechanisms in polar and/or nucleophilic sol-

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